ELLIPSOMETRIC METHODS IN ELECTROCHEMISTRY

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Ellipsometry is a useful tool to apply in the study of electrochemical reactions which involve film formation or dissolution. Ellipsometry is useful because it is very sensitive and because it may be applied in situ.

To understand ellipsometry, we must understand polarized light. Light is an electromagnetic wave and so is characterized by an electric and a magnetic vector. Since the electric vector and magnetic vector are always normal to each other, we need only consider the motion of the electric vector in our discussion. In linearly polarized light, the electric vector vibrates in a single plane. The inclination of the light may be described in terms of an angle, α. To define this ratio, in ellipsometry, it is convenient to take as our reference the directions normal and parallel to the test surface. Then:

$$\tan \alpha = E^p/E^n$$

where E^p is the amplitude of the parallel electric vector and E^n the amplitude of the normal vector.

When light is passed through certain materials, polaroid(quinine iodosulfate), for example, or through certain prisms (Nicol prism) only linearly polarized light vibrating in a certain plane is transmitted. When linearly polarized light is reflected or refracted at an interface between dielectrics (e.g., air-water), the plane of polarization is shifted causing a change in α.

Other materials, anisotropic materials, cause a phase shift in the components of light. Thus when linearly polarized light is passed through calcite, it is resolved into two components along its optical axes. These components travel at different velocities so that a phase shift is introduced between the components. When the light emerges from such a crystal it is no longer linearly polarized but is elliptically polarized. The tip of the electric vector no longer vibrates in a single plane, but rotates with time and traces out an ellipse. This ellipse is characterized by the angle of orientation of its major axis and the ratio of the two components.

An alternate way of characterizing the ellipse is in terms of the amplitude of two components normal to each other and the phase difference between them.

When polarized light is reflected from a conducting surface, both the amplitude ratio, $\tan \alpha$, and the phase are changed. Thus, reflection from a metal is similar to a combination of reflection from a dielectric and transmission through anisotropic material. For reflection from a metal, the two basic ellipsometric parameters are defined. The relative amplitude diminution:

$$\tan \psi = \tan \alpha_R/\tan \alpha_I$$

where $\tan \psi$ is the relative amplitude diminution and R designates the reflected beam and I the incident beam. The difference in phase of the two components is defined as:

$$\Delta = D_R - D_I$$

where Δ is the relative phase retardation, D_R is the phase difference of the normal and parallel components in the reflected beam and D_I is the same quantity for the incident beam.

When a film is present on the metal surface, the relation between Δ and ψ and film and metal properties becomes quite complex:

$$\tan \psi \exp(i\Delta) = \frac{\dfrac{r_{12}^p + r_{23}^p \exp(-2i\delta)}{1 + r_{12}^p r_{23}^p \exp(-2i\delta)}}{\dfrac{r_{12}^n + r_{23}^n \exp(-2i\delta)}{1 + r_{12}^n r_{23}^n \exp(-2i\delta)}}$$

where

$$r_{ab}^p = \frac{n_b \cos \varphi_a - n_a \cos \varphi_b}{n_b \cos \varphi_a + n_a \cos \varphi_b}$$

$$r_{ab}^n = \frac{n_a \cos \varphi_a - n_b \cos \varphi_b}{n_a \cos \varphi_a + n_b \cos \varphi_b}$$

and

$$\delta = \frac{2\pi n_2 \cos \varphi_2 L}{\lambda}$$

where n is the refractive index of the media (for absorbing media $n = \bar{n} + i\kappa$ where $\bar{n}$ is real part of the refractive index and κ an absorption coefficient), φ are the angles of incidence and refraction, L is the film thickness, λ the wavelength of the light, and the subscripts 1, 2 and 3 represent the medium, film and substrate, respectively. It is apparent that the relation between Δ and ψ and the film thickness and refractive index is complicated. It has only been since the development of modern electronic computers that the complete equations have been used in calculations. Approximate formulas, valid for very thin films (< 100 Å), were derived by Drude who also derived the complete expressions but found them too difficult to use.

When plots are made of ψ versus Δ as a function of film thickness, the relation is not complicated. For a transparent film a closed curve is obtained which repeats for each wavelength of thickness (λ/n). For an adsorbing film this curve is a spiral which ends at the ψ-Δ point which corresponds to the reflection from the film alone. This termination of the spiral results when the film is so thick that no light reflected from the substrate reaches the surface. The observed parameters must then be those for the film alone. For such thick films ellipsometry cannot be used to determine the thickness.

An alternative type of representation is the polar coordinate type of plot, in which Δ is the angle and $\tan \psi$ the radial distance.

The Application of Ellipsometry to Electrochemistry

To apply ellipsometry to electrochemistry, we must use an electrochemical cell. Thus, the light beam must pass through the cell walls into the solution and then back out again.

The basic criteria is that one must know what effect the cell and solution have on the polarization state of the light. For passage of polarized light through a dielectric-dielectric interface, we have the relation:

$$\frac{\tan \alpha_T}{\tan \alpha_I} = \frac{1}{\cos(\varphi_I - \varphi_T)}$$

where $\tan \alpha_T$ and $\tan \alpha_I$ are the amplitude ratio for the transmitted and incident beam and φ_I is the angle of incidence and φ_T is the angle of transmission. To have no change in $\tan \alpha$ at the interface is desirable. Hence, we must have $\varphi_I = \varphi_T$. For media of different refractive indices this can only occur for normal incidence. This arrangement is frequently used. It has the advantage that no corrections need be made for the cell. The major disadvantage of this method is that the angle of incidence is fixed.

The alternate method is to use rectangular cells and correct for the changes at the interfaces. These corrections are not complicated. Another correction which one must apply when working in solution is in the angel of incidence. If one is not working with windows normal to the light path, refraction will occur at the interfaces and thus change the angle of incidence. This is, of course, easily corrected by Snell's law. Neither normal windows or parallel windows offer a clear-cut advantage so that secondary considerations as whether the angle of incidence is to be varied or convenience in cell design will govern the choice.

Problems in applying Ellipsometry to Electrochemistry

a. Refractive index of the Metal: To interpret the changes in Δ and ψ upon film growth, one must know Δ^o and ψ^o, the values of Δ and ψ corresponding to the bare metal surface. In many cases it may prove difficult to experimentally obtain a bare metal surface in solution because of metal dissolution and spontaneous film formation. Electrochemistry can aid itself here by controlling the potential of the metal in a region in which the bare surface is stable. When this is not possible, one may use data obtained from high vacuum measurements for the bare surface.

b. The slowness of making measurements: Many electrochemical reactions occur quite rapidly so that it is desirable to make rapid ellipsometric measurements so that competing reactions do not distort the measurements. The manual adjustment of the ellipsometer requires about one minute. This is a very long time compared to electrochemical transients which are often carried out in a few milliseconds. Various types of automated ellipsometers are being made but thus far only give a response on the order of a second. In principle, much faster instruments are possible but require considerable sophistication in the optical and electronic components to give acceptable accuracy.

c. Interpretation of results: The interpretation of results obtained by ellipsometry can be quite difficult. Many electrochemically formed films are electronic conductors and hence absorb light. The films then possess three optical properties: thickness, real part of the refractive index and absorption coefficient. From a single measurement of Δ and ψ, these three quantities cannot be uniquely determined. Several methods of attacking this problem have been suggested. These may be either ellipsometric measurements or involve an independent method. The ellipsometric methods include varying the refractive index of the media, varying the substrate, varying the angle of incidence and varying the wavelength. Non ellipsometric methods are to determine n or κ from independent measurements on the film material and determining the amount of film by coulometry.

For very thin films (100 Å), the method of variation of film thickness with refractive index assumed constant does not succeed unless very precise (error $\ll 0.01^{\circ}$) measurements can be made. Since the error is typically greater than this, the method will generally not succeed. Also, for such very thin films, the refractive index is likely to depend on thickness. For films thicker than 100 Å, this method may succeed.

The method of varying the substrate while keeping the same film has been theoretically shown to be successful. In practice, for electrochemical measurements, this method could only be used for adsorbed films. For films formed from the substrate material, the method is not applicable. Also, it may prove experimentally difficult to produce films of the same thickness on different substrates.

Theoretical calculations have shown that the method of variation of the refractive index of the medium should also be a feasible method of obtaining a solution for n, κ and L. However, one must assume that no change occurs in the film as the media is changed - an assumption which may prove difficult to verify.

Calculatinns have shown that the method of variation of the angle of incidence may succeed in special cases but is not a general method.

The method of variation of wavelength may also be attempted. One complication which would enter is that κ will depend on the wavelength. This will give an additional variable so that a solution would probably not be possible.

The use of values of n or κ for bulk materials has been used with some success. Here, one must show that the thin film is the same as the bulk material on which the measurements were made. Also, for very thin films, it is probable that n and κ vary with thickness due to compression of the film.

The use of coulometry with ellipsometry can be used to restrict the range of possible thicknesses. Thus, by combining coulometry with ellipsometry the values of n, κ and L can be restricted.

The overall picture presented on the possibility of uniquely determining n, κ and L for thin films seems rather poor. In reality the situation is not nearly so bad. By restricting the values of n and κ to ranges which are experimentally found ($1 < n < 5$, $0 < -\kappa < 5$), certain restrictions on the film properties may be made. A minimum value of film thickness which is compatible with Δ and Ψ is usually found. Thus one can conclude that the film must be thicker than a minimum value. Also, light absorbing films are readily distinguished from transparent films.

The problem in inhomogeneous film has also received theoretical attention. Here it has been shown that the films are seen by the ellipsometer as a uniform film with an average thickness and refractive index.

<u>Summary</u>

Ellipsometry is a very sensitive tool which may be applied <u>in situ</u> to study electrochemical reactions involving films. In considering the use of ellipsometry, one should consider the problems in applying the method. These include the difficulty of obtaining the optical parameters of bare metals and the difficulty of analyzing light absorbing films. These problems are not insurmountable so that ellipsometry is becoming increasingly important in research.